

**NASA CONTRACTOR
REPORT**



NASA CR-608

0099412

TECH LIBRARY KAFB, NM

NASA CR-608

**LOAN COPY: RETURN TO
AFWL (WLIL-2)
KIRTLAND AFB, N MEX**

CONTAINMENT OF LIQUID ZIRCONIUM AND NIOBIUM CARBIDES ON GRAPHITE BETWEEN 3500° AND 4700° K

by J. A. Cahill and A. V. Grosse

Prepared by
TEMPLE UNIVERSITY
Philadelphia, Pa.
for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1966



0099412

NADA 01 000

CONTAINMENT OF LIQUID ZIRCONIUM AND NIOBIUM CARBIDES
ON GRAPHITE BETWEEN 3500° AND 4700° K

By J. A. Cahill and A. V. Grosse

Distribution of this report is provided in the interest of
information exchange. Responsibility for the contents
resides in the author or organization that prepared it.

Prepared under Lewis Work Order C-54468A by
TEMPLE UNIVERSITY
Philadelphia, Pa.

for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 - Price \$2.00

FOREWORD

This report covers research related to one aspect of advanced nuclear rocket propulsion. This work was performed under NASA Work Order C-54468A under the technical management of Maynard F. Taylor, Nuclear Systems Division, Lewis Research Center.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY-----	1
INTRODUCTION-----	2
DISCUSSION OF WORK PERFORMED-----	4
A. Materials-----	4
B. Apparatus-----	5
1. Rotating Double Arc Furnace-----	5
2. Crucible Configuration-----	8
3. Sample Preparation-----	8
C. Procedure-----	9
1. Analysis of Carbides-----	10
a. Combustion Method	
b. X-ray Studies	
2. Temperature Measurements-----	11
D. Description of Tests-----	15
1. Run 1 - ZrC-I-----	15
2. Run 2 - NbC-I-----	19
3. Run 3 - ZrC-II-----	21
4. Run 4 - NbC-II-----	25
5. Run 5 - NbC-III-----	28
E. Results and Conclusions-----	29

SUMMARY

Three niobium and two zirconium carbide liquid pipes approximately 4.5 cm long X 3 cm. i.d. X 0.5 cm wall were contained in rotating graphite crucibles at temperatures between 3800° and 4700°K for periods between 2 and 10 minutes. The heat source used was the rotating double arc furnace of the Reynolds Metals Company operated in a helium atmosphere.

The increase in carbon content of the carbide pipes under the conditions of these tests and the recession (i.e., decrease in wall thickness of the graphite crucibles supporting the carbides) caused by the sublimation and solubility of the graphite were measured. Present results indicate the order of magnitude one can expect for this recession if pure graphite is used as a crucible or pipe material to contain the carbides is about 0.1 mm/min. or 6.0 mm/hr.

INTRODUCTION

In accordance with Amendment No. 1 dated February 19, 1965 to Requisition No. C-54468-A from the Lewis Research Center of the National Aeronautics and Space Administration to the Reynolds Metals Company, five tests described herein with zirconium and niobium carbides were made at the Research Institute of Temple University. It was agreed that the centrifugally rotating double carbon arc furnace developed for the Reynolds Metals Company by the Research Institute of Temple University (see Fig. 1) would be used for these tests. Previously, this furnace was used to contain carbides such as tantalum and tungsten as liquids at temperatures between 4000° - 5000° K for short periods of time (2-10 min.)(1). The present tests with zirconium and niobium carbides were performed to establish that they could be contained on graphite in the above furnace at temperatures between 3400° - 4700° K for time periods possibly extending up to one-half hour. The rotating double arc furnace was designed to operate in the range of 20 Kw for 5 minute periods or at a heat input of 5700 BTU and operating the furnace, e.g., even at 10 Kw for a period of 30 minutes would involve a heat input of

17,000 BTU or three times greater. Therefore, the present runs were made for as long a period as possible at the desired temperatures and were halted whenever the furnace became overheated.

This report presents in a concise manner the results obtained. These results were presented in several previous reports from the Reynolds Metals Company to the Lewis Research Center, National Aeronautics and Space Administration.

DISCUSSION OF WORK PERFORMED

A. Materials

The zirconium carbide powder from Shield Alloy Corp., Newfield, N. J., had the composition:

Zr	88.31 wt.%
C	11.61 wt.% (0.2 wt.% free carbon)
Hf	0.008 wt.%
Fe	0.02 wt.%
Si	<u>0.01 wt.%</u>
	99.96 wt.%

This material was used in both zirconium carbide runs (Runs #1 and 3).

Niobium carbide having the composition:

Nb	86.0 wt.%
Ta	2.0 wt.%
Ti	0.6 wt.%
Total C	11.0 wt.%
Free C	0.1 wt.%
Fe	0.1 wt.%
Si	0.03 wt.%
Ca	<u>0.03 wt.%</u>
	99.76 wt.%

was used in the first niobium carbide run (Run #2) because of its availability. A much purer grade of NbC, also obtained from Shield Alloy Corp., was used for the second and third niobium carbide run (Runs #4 and 5). It

had the composition:

Nb	88.68
Fe	0.09
Ta	0.11
Ti	0.01
Total C	11.07
Free C	0.10
Chlorination Residue	<u>0.04</u>

100.00

and had a much lower tantalum content (0.11 wt.%) than the NbC used in Run #2 (2.0 wt.%).

B. Apparatus

1. Rotating Double Arc Furnace: The test samples were run in the rotating double arc furnace (Fig. 1) designed and built at the Research Institute of Temple University for Reynolds Metals Company. High temperatures are produced in this furnace by means of two arcs which are struck between the graphite electrodes and the carbide sample held in a rotating graphite tube. The arcs were powered by two Airco 600 ampere, 16 Kw welders; the carbide specimens were made the anodes (+ ground) while the graphite electrodes were used as cathodes. The furnace (Fig. 2) is rotated by a one-horsepower variable drive unit having an rpm range from 500 to 1500 rpm. The annular space between the graphite support tube and steel drum is filled

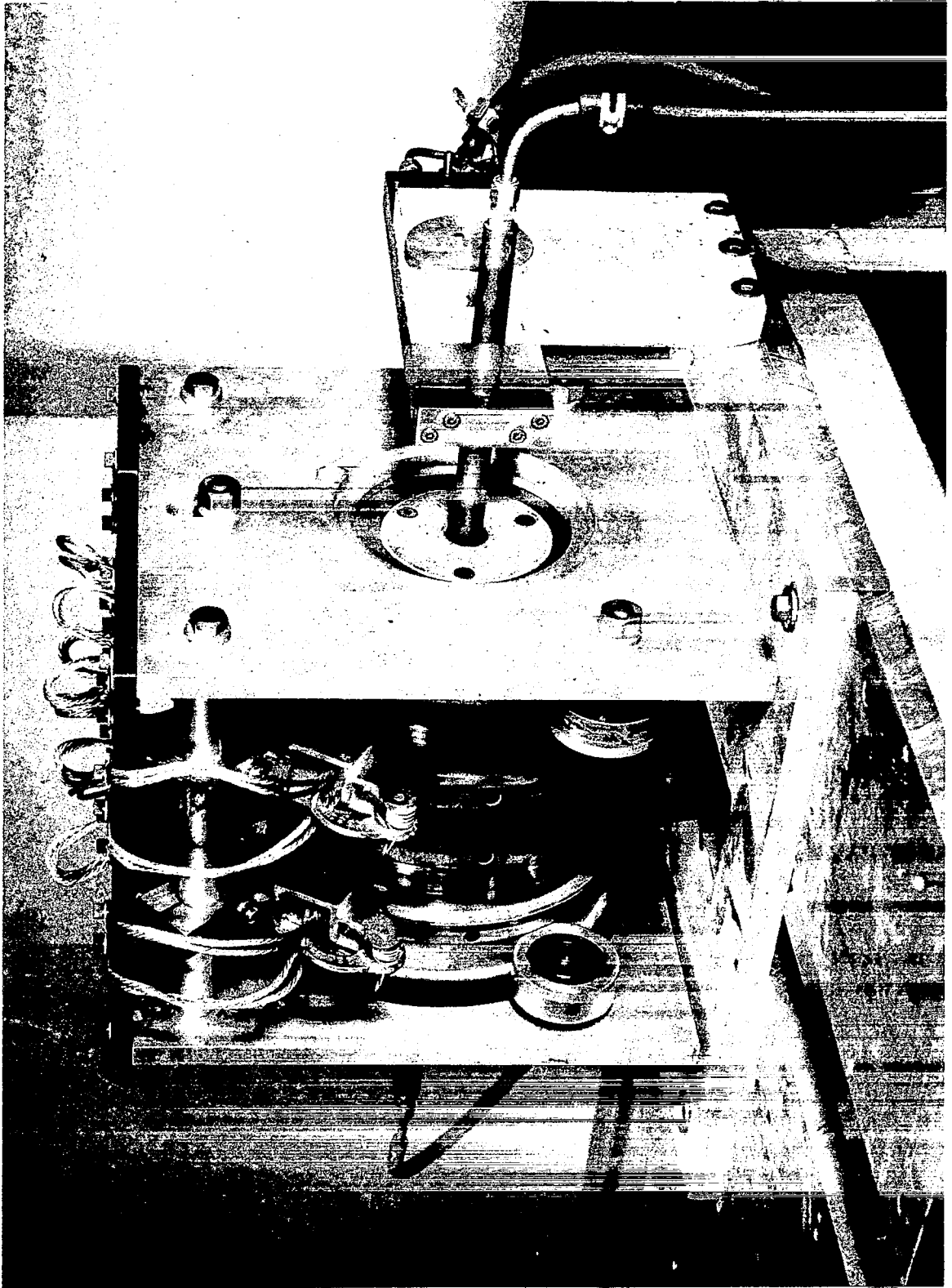
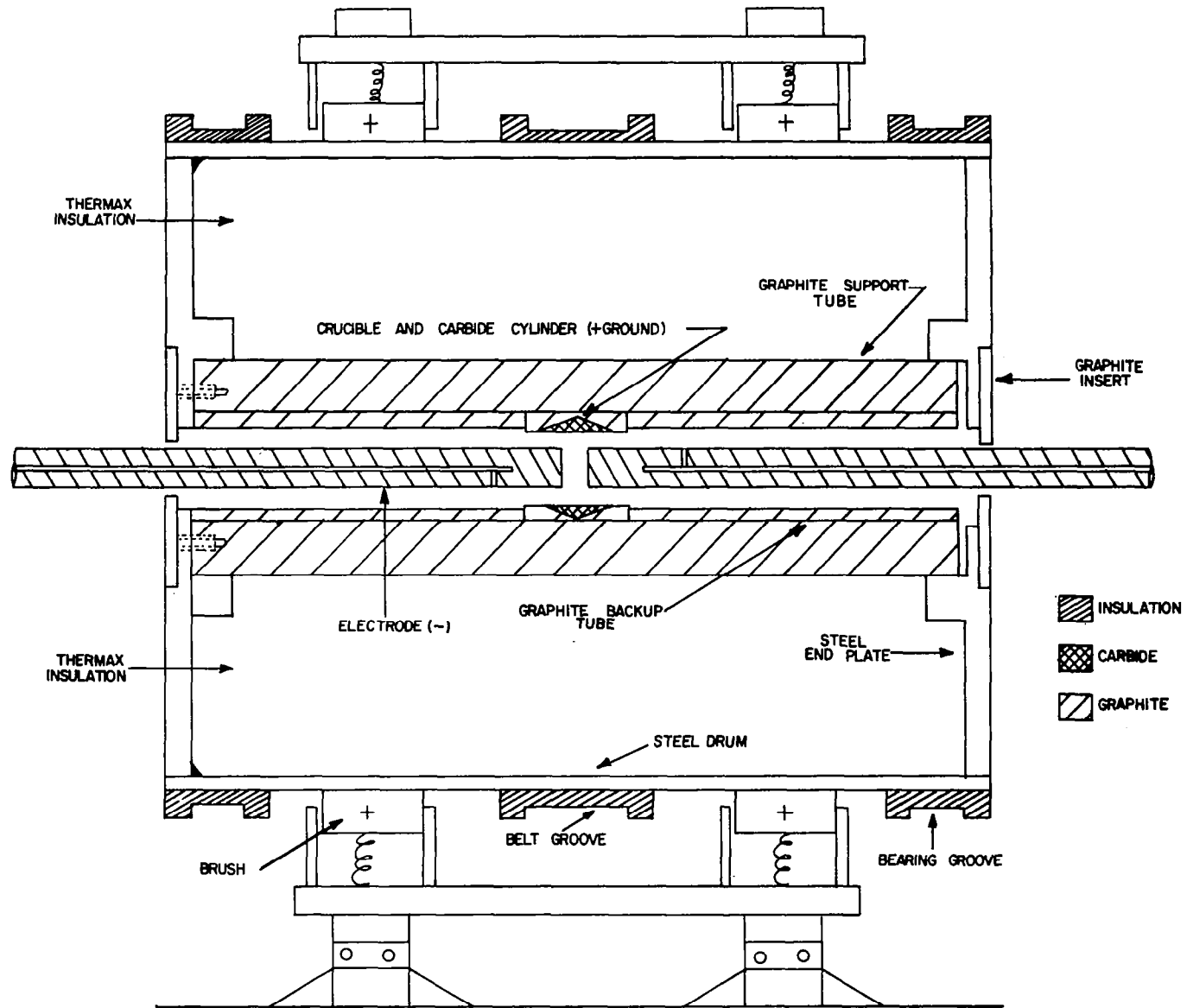


FIGURE 1

ROTATING ARC FURNACE

ROTATING ARC FURNACE
FIGURE 2



with a special insulating carbon black called Thermax. The graphite backup or spacer tubes and graphite pipe containing the carbide slide-fit the 1-3/4 in. i.d. graphite support tube and are held in place by the graphite inserts and end plates. The graphite electrodes, 1/2"-3/4" o.d., are held concentrically in the carbide pipe about 1/2" apart and operate from 8 to 15 Kw with a range from 20-40 volts and 300-600 amps. Helium is passed through each electrode at 2200 cc/min. using a separate flowmeter for each electrode.

2. Crucible Configuration: The graphite crucibles or pipes used to contain the carbides (see Fig. 1) were tapered on the inside diameter, forming a v-shaped crucible. This design tended to pool the liquid carbides over the apex of the crucibles.

3. Sample Preparation: The v-shaped crucibles were charged with a parrafin oil-carbide slurry which was centrifugally cast in the crucible at 2800 rpm. During the casting operation ends were provided to hold the slurry in the crucible and the oil which was forced to the surface was removed by stroking the carbide surface with a soft rubber blade. After heating to 2200°K for 4 hrs., the

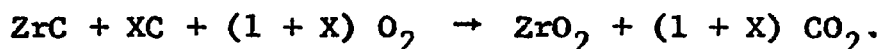
carbide pipe thus formed had a porosity of about 40%. A few longitudinal cracks usually were present in the cylinders but they did not seriously affect the performance of the pipes.

C. Procedure

A known amount, between 30 and 85 g., of carbide was cast into a graphite v-shaped crucible, sintered and placed in the rotating double arc furnace. The furnace was rotated to the desired rpm (varied from 455 to 1000) and the arcs initiated with the high frequency starting circuit in the welders. Helium was flushed through the electrodes to purge the system and just prior to start-up the helium flow was reduced to about 2200 cc/min. per electrode. During a run, temperature measurements were made on the surface of the carbide sample with an optical pyrometer. The weight loss of the carbide and crucible, the recession of the crucible wall and final composition of the carbide were measured. Power input, crucible shape, sample weight, rpm's and run time were varied to produce the requested run conditons with the available equipment.

1. Analysis of Carbides Tested

a. Combustion method: From each carbide melt an average sample of approximately 2 g. was analyzed. The sample was ground to a fine mesh size and combusted with oxygen in an electric furnace. The wt.% gain of the sample can be related to the percentage of carbon from the equation, e.g., for ZrC:



The results of the analysis for each sample are given in Part D of this report and in Table VI.

b. X-ray studies: X-ray diffraction studies usually permit a more detailed analysis of the components. However, the patterns of the carbide samples showed essentially only the lines of the pure carbides. Graphite could not be detected with our x-ray apparatus in mixtures having the above carbon concentrations. To check this point, an x-ray diffraction pattern was taken of a mixture of ZrC + 2.36 C and only the lines of pure ZrC could be observed. Pure graphite on the other hand, when analyzed, gave the expected lines. The large difference in densities between the carbides (NbC and ZrC) and C could be responsible for masking the graphite lines.

2. Temperature Measurements: The temperature was measured with an optical pyrometer (2) of the disappearing filament type from Pyrometer Instrument Company that had been calibrated previously at the platinum point (2043°K), the boiling points of several metals (3) and at the apparent temperature of the standard carbon arc ($3820 \pm 15^{\circ}\text{K}$) (4). The inside of the furnace could be seen through a notch cut in the rectangular copper block which held one electrode. Using goggles one could distinguish, by sighting through this notch, the two electrodes, the graphite backup tube, the smaller diameter graphite pipe and the surface of the carbide pipe itself.

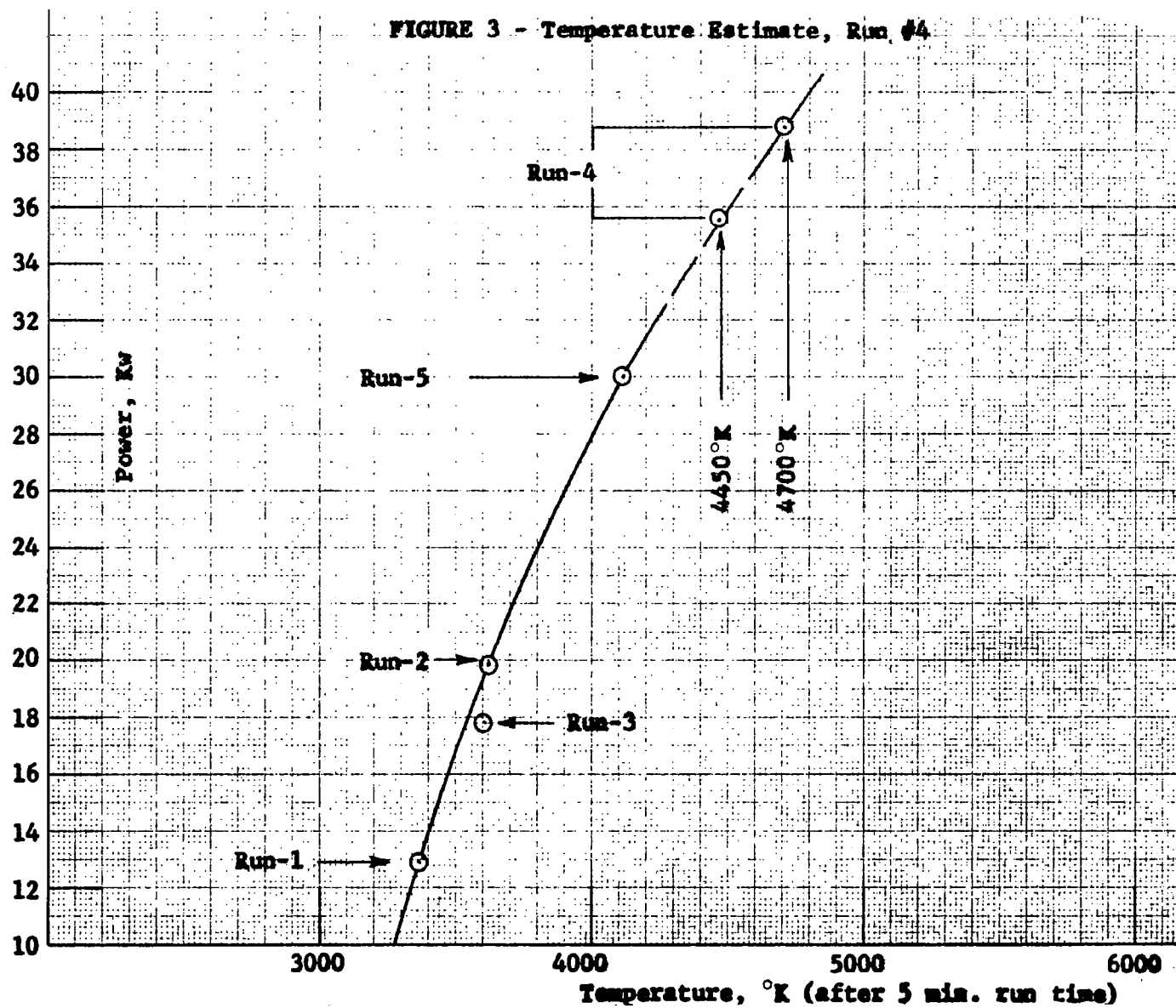
The graphite vapor which evaporated from the electrodes and condensed on the cooler interior furnace surfaces at temperatures below 3900°K did not interfere with temperature measurements in this range. However, at temperatures $> 3900^{\circ}\text{K}$ and high current densities the rate of graphite evaporation increased and carbon vapor condensed in the helium stream. This graphite was carried out of the furnace as soot, thereby interfering with temperature measurements. In the $3800\text{-}4100^{\circ}\text{K}$ range, temperature measurements could only be made when the atmosphere would clear momentarily. Temperatures reached above 4100°K , e.g., in

Run #4 had to be estimated because of the sooty atmosphere. This difficulty could easily be overcome by providing a helium or argon purge to blow the soot out the other end of the furnace.

Figure 3 shows how the high temperature limits of 4400-4700°K were estimated for Run #4. Since the power inputs for the various runs during the initial 5-1/2 min. were reasonably constant for Runs #1 to #5 and the temperatures reached after this time were known, the power input vs. temperature plot shown in Fig. 3 could be made. A smooth curve is formed covering inputs from 13 Kw to 30 Kw and temperatures between 3300°K and 4100°K. Actually, by increasing the power by a factor of three, i.e., from 10 Kw to 30 Kw, the temperature increased by 25% in the 5 min. interval.

A consideration of the inside carbide diameter, furnace length and geometry of inner furnace surfaces showed that black body conditions were probably not ideal in these experiments. The temperature of an empty graphite crucible was uniform over its 5 cm length when heated in the 3400-3800°K range. Uniform temperatures must also prevail over this length with carbide in the crucible because of the high thermal conductivity of

FIGURE 3 - Temperature Estimate, Run #4



both the carbide and graphite. At temperatures above the sublimation point of graphite (3900°K) (5) one can expect differences between the carbide and graphite temperatures because the temperature of the carbon cannot be greater than its sublimation point (\approx 3900°K) at 1 atm. pressure. The apparent temperature of the carbide and graphite pipes up to 3900°K as observed with the optical pyrometer in these tests was the same. If the spectral emissivity of the carbide was in the range of .64-.52 as reported (6) for pure ZrC in the 2100-2670°K temperature range at a true temperature of 3700°K then the apparent temperature of the carbide should have been at least 330° lower than the apparent graphite temperature. The high carbon content of the carbides, 64 at.% in NbC and up to 77 at.% in ZrC, may have shifted their emissivities closer to the spectral emissivity of graphite. In view of the above the temperature measurements of the carbides were tentatively corrected using an emissivity value of 0.85. If ideal black body conditions did in fact exist the corrections would involve an error in the reported temperature of only 80°K, or 2%, at 3600°K.

D. Description of the Tests

1. Run 1 - ZrC-I: A zirconium carbide sample was held in a rotating graphite pipe at temperatures exceeding 3500°K for four minutes. The temperature was measured with an optical pyrometer and at four minutes before the end of the run it was 3500°K. It then gradually increased to 3800°K.

Excessive sublimation of graphite, as evidenced by smoking and the power unsteadiness of the arcs, made a shutdown advisable at the end of nine minutes. All of the zirconium carbide was melted and the original sample (mass=53.40 g.) was essentially all recovered. The test conditions of the run are shown in Table I.

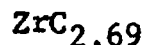
TABLE I

Time, Minutes	Start	1'45"	3'0"	4'0"	5'0"	6'30"	7'30"	8'45"
Electrode I								
Amps	300	200	275	275	350	375	275	200
Volts	28	34	28	28	30	30	40	40
Kw	8.4	6.8	7.7	7.7	10.50	11.25	11.00	8.0
Electrode II								
Amps	300	100	200	200	300	300	250	200
Volts	20	36	28	25	30	34	40	44
Kw	6.0	3.6	5.6	5.0	9.0	10.2	10.0	8.8
Total Power, Kw	14.4	10.4	13.3	12.7	19.5	21.4	21.0	16.8

RPM = 555

Helium Flow = 2200 cc/min.

The total carbon content of this sample was 26.17 wt.% or 72.93 at.% C which corresponds to the formula:



The final solid ZrC-carbon mixture had a porosity of about 17% caused by the voids created when the liquid pipe cooled. From the well-known WADA "Thermophysical Properties" book (7), thermal expansion data and the x-ray density, 6.44 g/cc. at 20°C were obtained and a solid density at the melting point (3450°K) was estimated as 6.06 g/cc. Assuming an approximate 10% expansion on melting, the liquid density at the melting point was calculated as 5.51 g/cc. This is not to say the carbide liquid had this density because due allowance should be given to the graphite present in the liquid at operating temperatures.

Figure 4 shows the ZrC melt cut in half perpendicular to its axis of rotation. In a number of places the ZrC crystallized in shiny metallic-looking thin platelets of about 1/2 mm in size. Examination of the crucible wall at the apex indicated that the original wall thickness of the apex of the crucible (≈ 2.2 mm) was reduced to ≈ 1 mm. Sublimation and/or solubility of the graphite are the possible causes for this reduction in

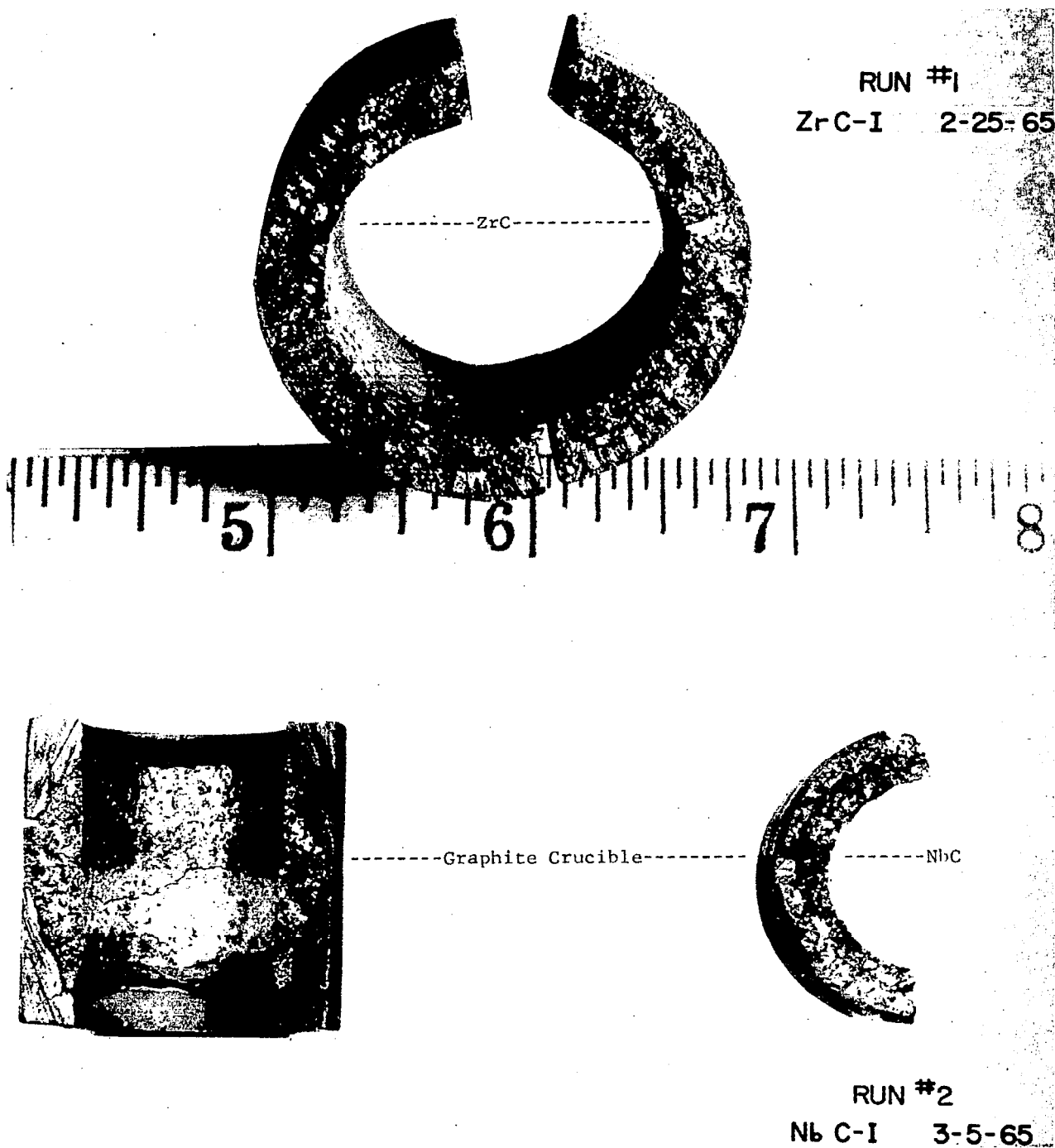


FIGURE 4

crucible wall thickness. It should be mentioned that special experiments would be necessary to determine the relative extent of these two causes. The solubility of carbon in uranium, zirconium and iron at temperatures up to 3200°K (8) has been determined at the Research Institute of Temple University and a suitably designed rotating furnace that would operate above the sublimation point of graphite could be used to determine the solubility of carbon in ZrC from the melting point to \approx 4500°K. Here the technique of taking "grab" samples directly at the experimental conditions instead of after solidification could be used as described in connection with the solubility of carbon in liquid iron which appeared recently (9).

Solubility studies could be carried out in a more conventional way by using a nonrotating type furnace such as the one discussed recently (10). A specially constructed graphite crucible which would allow the liquid carbide to be sampled at some predetermined time would replace the one described above.

2. Run 2 - NbC-I: A niobium carbide sample was held in a rotating graphite pipe at temperatures between 3300° and 3900°K for six minutes in a total run time of eight minutes. After cooling, the niobium carbide charge (mass=85.81 g.) which had been completely melted during the run was essentially all recovered together with its graphite pipe insert. The test conditions are given in Table II.

TABLE II

Time, Minutes	Start	2'0"	3'0"	4'30"	7'0"	7'30"	8'0"
Electrode I							
Amps	150	360	500	450	300	300	---
Volts	30	32	24	24	34	34	---
Kw	4.5	11.5	12.0	10.8	10.2	10.2	---
Electrode II							
Amps	200	350	470	450	270	270	---
Volts	34	32	23	24	36	36	---
Kw	6.8	11.2	10.9	10.8	9.7	9.7	---
Total Power, Kw	11.3	22.7	22.9	21.6	19.9	19.9	---

RPM = 555

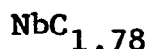
Helium flow = 2200 cc/min.

The power per arc was closely regulated and nearly equal, particularly after the initial three minutes.

The graphite pipe originally had a wall thickness of about 2.2 mm at its apex. This was reduced to 1.0 mm (at the cross section being investigated) during the run by solubility and/or sublimation and resulted in a 3 g. weight loss. Distinct boundary between the graphite pipe and NbC was visible and a photograph of the sample is shown in Fig. 4. A thin gray coating of graphite was observed on the bottom of the cavities which formed when the NbC cooled. The gray graphite coating was scraped off and metallic-looking NbC could be seen beneath it. This graphite could have formed in these places as the solidification point of the melt was reached.

The liquid density of pure NbC at the melting point was calculated as 6.61 g/cc. from a solid density at the melting point (3750°K) of 7.27 g/cc. and an assumed expansion on melting of 10%. The melting point solid density was estimated from the thermal expansion coefficients listed by Goldsmith, et al. (7), and the x-ray density at room temperature, 7.85 g/cc. (11). The actual density of the carbide mixture with graphite will, of course, differ from the above densities since they were calculated for pure NbC, e.g., ideal mixing of .80 moles of carbon with 1 mole of NbC would change the melting point liquid density from 6.61 g/cc. to \approx 6.25 g/cc.

An average sample (500 mg.) of the carbide carbon mixture was analyzed as described for Sample No. 1, namely, by determining its weight change on ignition in oxygen. The free carbon and the weight of the NbC present in the mixture were calculated from the sample's weight gain on ignition and the ratio of the Nb, Ta and Ti present in the original material. The small effect that the presence of Ta and Ti had on the weight gain of the sample was thereby eliminated and gave a result equivalent to the one that would have been obtained if pure NbC were used in the run. On this basis, the sample contained 18.75 wt.% C or 64.2 at.% C and would correspond to the formula:



3. Run 3 - ZrC-II: About 30 g. of liquid zirconium carbide was contained in a graphite pipe at temperatures between 3700-4000°K for 10 minutes. A photograph of the graphite pipe and melted carbide after the run is shown in Fig. 5.

The longer run time and higher temperatures anticipated in this second ZrC run prompted the following changes on the apparatus: (1) The end plate insulations

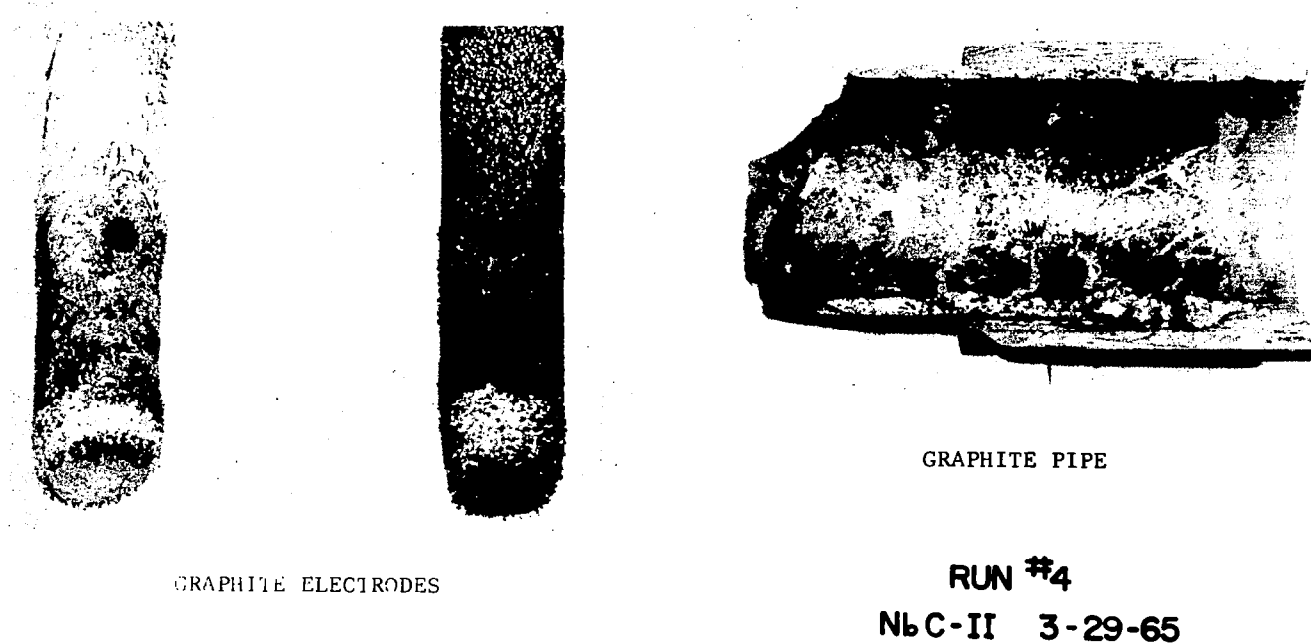
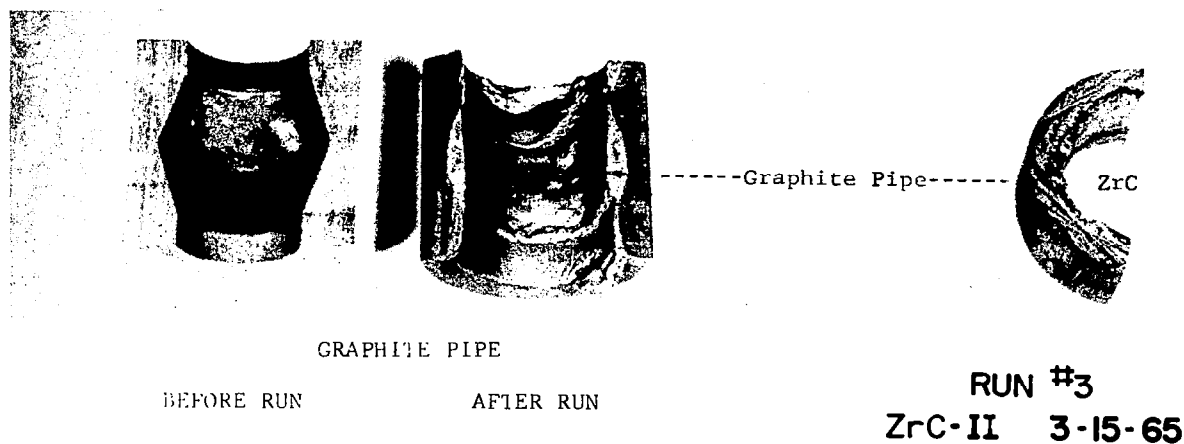


FIGURE 5

(see Fig. 1) were made of graphite to withstand higher temperatures than the transite inserts used in the first ZrC run and (2) the graphite pipe (see Fig. 1) used to contain the carbide was provided with a 6 mm wall thickness at its apex compared to the 2 mm apex wall previously used. The above changes made on the apparatus permitted us to run for 8 minutes instead of 2 minutes above 3700°K as in the first ZrC run. The graphite end plate inserts reached and withstood 900°K, a temperature which would have melted transite inserts and caused the run to be halted. The heat transferred to the steel drum during the course of the run caused its exterior insulation to smoke heavily. And, 10 minutes after the run, rotation of the drum had to be stopped when the insulation began to break apart. Test conditions of this run are given in Table III.

On the average only 2.0 ± 0.1 mm of wall was dissolved or sublimed in 10 minutes at 3700-4000°K in this run compared to 1.0 ± 0.1 mm wall thickness loss in four minutes at 3300-3800°K in the first ZrC run. The long duration of the run caused the shoulders of the crucible to sublime and hence permitted about 10 g. or

TABLE III

Time, Minutes	Start	2	5' 30"	6' 30"	7' 30"	9' 30"	11' 0"	12' 15"	14' 0"	15' 0"
Electrode I										
Amps	330	350	300	300	200	150	150	200	100	150
Volts	24	24	30	30	40	44	44	40	46	60
Kw	7.9	8.4	9.0	9.0	8.0	6.6	6.6	8.0	4.6	9.0
Electrode II										
Amps	200	350	340	300	230	150	150	120	100	100
Volts	24	24	26	30	40	44	44	40	46	46
Kw	4.8	8.4	8.8	9.0	9.2	6.6	6.6	4.8	4.6	4.6
Total Power, Kw	12.7	16.8	17.8	18.0	17.2	13.2	13.2	12.8	9.2	13.6

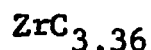
RPM = 555

Helium flow = 2100 cc/min. per electrode

1.5 cc of the liquid carbide (volume 4.7 cc) to run out of the crucible onto the backup tubes. This effect could be easily avoided by making the carbide charge longer and/or deeper so the crucible shoulders would be further away from the high temperature zone.

The sample was covered with two distinct layers. The upper one consisted of \approx 0.8 g. of pure graphite which was moulded together and formed a thin crust 0.3 mm thick. Under this was a second softer layer about 0.1 mm thick which contained 26.20 wt.% C and 73.80 wt.% ZrC. Beneath

these two layers was the surface of the bulk of the carbide. An average sample of this material was analyzed by combustion in oxygen and measurement of its weight change, and also by x-ray analysis. The average sample of the carbide was found to contain 30.70 wt.% C or 77.06 at.% C which corresponds to:



4. Run 4 - NbC-II: This niobium carbide sample was held in a rotating graphite pipe between 4400-4700°K for a few minutes during a total run time of 5-1/2 minutes. After cooling, the sample (wt.=77.3 g.) which had completely melted, solidified in the crucible and on the graphite backup tube. A photograph of the carbide and crucible is shown in Fig. 5. Table IV, which lists the test conditions, shows that in the final two minutes of operation the power was increased to 39 Kw. This resulted in the formation of a Beck arc. The high-intensity Beck arc had the undesirable effect of evaporating the shoulder from one side of the graphite pipe and caused the NbC to run onto the adjoining graphite backup tube. Thus, the electrodes, crucible and carbide

TABLE IV

Time, Minutes	0	1	2	2 $\frac{1}{2}$	3 $\frac{1}{2}$	5	5 $\frac{1}{4}$	5 $\frac{1}{2}$
Electrode I								
Amps	300	400	450	450	500	650		750
Volts	50	30	35	30	32	30	Both	20
Kw	15	12	15.7	13.5	16	19.5	arcs	15
Electrode II								
Amps	100	400	450	500	550	650	un-	650
Volts	30	30	35	30	36	30		30
Kw	3.0	12	15.7	15	19.8	19.5	steady	19.5
Total Power, Kw	18.0	24.0	31.4	28.5	35.8	39.0	-----	34.5

RPM = 550

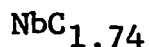
Helium flow = 2200 cc/min (thru 5/8" diameter electrodes)

all gave the appearance of having been subjected to much more drastic conditions than in any of the previous runs. The NbC crucible and electrodes are shown before and after the run in Fig. 5. The apex of the graphite pipe, originally 3.17 mm thick, was reduced by only about 0.1 mm during the run. This low recession appears to be inconsistent with the other pipe recessions which ranged from about 0.4 to 0.9 mm at lower temperatures. The small recession could have been caused by the overall more drastic run conditions in addition to the individual or collective influence of the following factors: (1) the

high concentration of carbon in the vapor phase due to the Beck arc, (2) the spreading of the liquid carbide over an area approximately twice that of the other runs and (3) the possibility that the much higher carbide temperature formed an insulating cushion of carbon vapor between itself and the adjacent graphite pipe.

The temperature increased steadily to 3630°K during the first 2 minutes of the run. The power was then increased to 36 Kw after 2-1/2 minutes and fluctuated between 36 and 39 Kw until 5 minutes of run had elapsed. During this latter period the graphite that was being evaporated from the electrodes came out of the furnace as soot and prevented accurate temperature measurements; temperatures between 4400-4700°K must have been reached. See pages 13 and 14 for further explanation.

An average sample of the carbide was combusted in oxygen and from its weight change its carbon content determined as 18.35 wt.% C. This corresponds to 63.49 at.% C or the formula:



5. Run 5 - NbC-III: Approximately 77.2 g. of Grade I NbC was contained in a graphite pipe at temperatures between 3800-4100°K for 3-1/2 minutes in a total run time of 5-1/2 minutes. This run appears to be the best of the NbC sample tests. Although run at a lower temperature than Run #4, it was better controlled from the standpoint of containment, as the weight loss of graphite pipe and carbide was only 0.23 g. compared to an 8.1 g. loss in Run #4. Moreover, no Beck arc was formed since a power input of approximately 30 Kw was maintained for the entire run time. Test conditions are summarized in Table V.

TABLE V

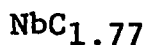
Time, Minutes	1.5	2	2.45	3.15	3.45	5	5.5
Electrode I							
Amps	550	500	450	500	450	475	475
Volts	28	28	30	30	30	30	30
Kw	15.4	14.0	13.5	15.0	13.5	14.2	14.2
Electrode II							
Amps	550	500	450	500	450	450	450
Volts	28	28	30	30	30	32	34
Kw	15.4	14.0	13.5	15.0	13.5	14.4	15.3
Total Power, Kw	30.8	28.0	27.0	30.0	27.0	28.6	29.5

RPM = 550

Helium Flow = 220 cc/min. per electrode (3/4" electrodes)

Since the power was held steady at approximately 30 Kw throughout this run, the temperature gradually increased from 3250°K after one minute of operation to a maximum value of 4095°K reached just before shutdown. One minute after the run the temperature had fallen to 3500°K and dropped to 2500°K three and one half minutes later.

An average sample of the carbide was combusted in oxygen and from its weight change the composition of the sample calculated to be 18.65 wt.% C. This composition corresponds to 63.93 at.% C or



A photograph of the graphite electrodes crucible and carbide pipe are shown in Fig. 6.

E. Results and Discussion

The principal objective of this work, namely, to contain liquid ZrC and NbC as "liquid pipes" inside subliming graphite pipes in the double arc rotating furnace over the temperature 3400-4700°K, has been accomplished. Recession rates, i.e., the rate of decrease of the graphite pipe wall thickness caused by sublimation

RUN #5

Nb C-III 3-29-65



FIGURE 6

and solubility, were also measured and the average value for the five runs is in the range of 0.1 mm/min or 6 mm/hr.

Table VI lists the weights of the carbides contained under the various test conditions. From the standpoint of containment, Run #5 is the best. This is mainly because the high intensity Beck arc was avoided and the electrodes were kept over the center of the carbide pipe. Table VII summarizes the test conditions, the corresponding carbide compositions, after cooling, and recession rates. The recession rate was not calculated for Run #4 because the drastic conditions that prevailed here limited the recession for reasons described in detail on p. 27 to only 0.1 mm. Recession of the graphite pipe is caused by both (a) solubility and (b) sublimation. At temperatures below 3500°K where the vapor pressure of carbon is < 30 mm the recession can be attributed mainly to solubility of the graphite pipe in the carbides. As the temperature of the carbide is raised to the sublimation point of graphite, 3900°K and above, sublimation becomes an important factor in governing the recession rate. The vapor pressure of carbon in solution should not be lowered

TABLE VI—Weight losses of carbides, crucibles and electrodes.

Sample Test	Carbide Weight, grams	Weight Loss of Carbide and Crucible, grams	Electrode Diameter	Electrode Weight Loss, grams	Time at Maximum Temperature, °K	Remarks
Run #1 ZrC-I	53.40	6.1	1/2"	6	4 min. 3300-3800°	Carbide contained in graphite pipe
Run #2 NbC-I	85.80	3.0	1/2"	4.2	2.5 min. 3800-3950°	Carbide contained in graphite pipe
Run #3 ZrC-II	30.01	16.0	1/2"	2.7	10 min. 3700-4000°	Crucible shoulder eroded. Carbide spilled onto backup tube
Run #4 NbC-II	77.30	8.1	5/8"	8.9	2 min. 4300-4700°	Beck arc produced. Crucible eroded. Carbide spilled. Electrodes eroded.
Run #5 NbC-III	77.20	0.23	3/4"	5.0	3-1/2 min. 3800-4100°	Carbide contained in graphite pipe

TABLE VII—Summary of test runs with zirconium and niobium carbide

Sample	Run Time, Minutes	Time at Maximum Temperature, °K	Maximum Power, Kw	Crucible Wall at Apex			Composition of Carbide Pipes after Cooling		
				Initial Thickness, mm	Recession				
					mm	mm/min	Wt.% C	At.% C	Metal-Carbon Ratio
Run #1 ZrC-I	9	4 min. 3300-3800°	13	2.37	0.1	0.1	26.17	72.93	ZrC _{2.69}
Run #2 NbC-I	8	2.5 min. 3800-3950°	20	2.37	0.9	0.11	18.75	64.20	NbC _{1.78}
Run #3 ZrC-II	15	10 min. 3700-4000°	18	6.0	2.0	0.13	30.70	77.06	ZrC _{3.36}
Run #4 NbC-II	5½	2 min. 4300-4700°	34-39	3.17	0.1	*	18.35	63.49	NbC _{1.74}
Run #5 NbC-III	5½	3.5 min. 3800-4100°	30	3.17	0.4	0.07	18.64	63.90	NbC _{1.77}
Average rate = 0.1									

(*) Excluded for reasons discussed on pp. 27 and 30.

significantly by the higher boiling carbides, $bp = 7500^{\circ}K$, because of the high concentration of carbon in the carbide-carbon solutions, i.e., 60-80 at.% C.

The weight loss of the carbide caused by overfilling the graphite pipe or crumbling of the carbide pipe during rotation prior to melting was reduced from 5 g in the first run to 0.23 g in the final, or fifth, run.

The present recession rate obtained of about 6 mm/hr is based on short run times and the use of pure carbides and graphite. A number of means both mechanical and chemical could be employed to reduce the recession to a minimum value. For example: (1) It would be of interest to study the recession rates using samples to which graphite has been added in amounts expected at the temperature selected, e.g., in Run #1 (see Table VII) the mixture of one mole ZrC to 1.69 g.atoms C would be used at $3800^{\circ}K$. This is not to imply that $ZrC_{2.69}$ would be the composition at temperature merely because it was the composition of the cooled carbide. It is not possible to safely make any conclusions regarding the composition at temperature based on the above since in addition to being in a graphite pipe at and above its sublimation point the

carbide is being exposed to the graphite vapor on its inner surface from the evaporating electrodes. One method available to determine the carbon composition at temperature would be to use the Research Institute's "grab sample" technique recently described in connection with the solubility of carbon in liquid iron to 3150°K (9). In the present circumstances a tungsten sample tube could be used to take a "grab sample" of the carbide-carbon solution at the operating temperature.

(2) In order to establish the amount of recession that would take place for a run time of, say, 30 min. the same sample could be run possibly six times for 5 min. duration at the desired temperature. This technique would remove the present time restriction on the double arc furnace.

(3) Recession rates as originally stressed (2) could be reduced by incorporating less volatile additives, such as metallic carbides and/or borides, into the graphite crucible or pipe, e.g., during their formulation, formation and manufacture.

(4) The undesirable effects produced when graphite electrodes are used at high power inputs could be avoided by using water-cooled metal or metal carbide electrodes which could be operated for substantially longer periods of time than presently possible.

(5) The construction of a furnace capable of withstanding the heat input for longer than 5 min. obviously would be of great importance for the study and interpretation of recession rates.

REFERENCES

1. A. V. Grosse and J. A. Cahill, Third Report on High Temperature Research Project for Reynolds Metals Company, Research Institute of Temple University, Philadelphia, Pa., June 25, 1965.
2. D. R. Lovejoy, "Accuracy of Optical Pyrometry in the Range 800° to 4000°C", Can. J. Phys., 36, 1397 (1958).
3. A. D. Kirshenbaum and J. A. Cahill, J. Inorg. Nucl. Chem., 26, 206 (1964).
4. "Temperature, Its Measurements and Control in Science and Industry", American Institute of Physics, Reinhold Publishing Co., New York, 1947, pp. 1141-49.
5. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements", Adv. in Chem. Series 18, A.C.S., Washington, D. C., 1956.
6. T. R. Riethof and V. J. DeSantis, Symposium on Thermal Radiation Properties of Solids, September 5-7, 1962, NASA SP-31, p. 565.
7. A. Goldsmith, T. E. Waterman and A. J. Hirschorn, "Thermophysical Properties of Solid Materials, Vol. I, WADA Tech. Report 58-476, August 1960.
8. A. D. Kirshenbaum and A. V. Grosse, Fifth Annual Report to the Atomic Energy Commission, Basic Research in Inorganic and Physical Chemistry at High Temperatures, Contract AT(30-1)-2082, Research Institute of Temple University, Philadelphia, Pa., June 30, 1963.
9. J. A. Cahill, A. D. Kirshenbaum and A. V. Grosse, Am. Soc. Metals, Trans. Quart., 57, 417 (1964).

10. A. V. Grosse and P. J. McGonigal, Second Report on High Temperature Research Project for the Reynolds Metals Company, Research Institute of Temple University, Philadelphia, Pa., April 30, 1964.
11. G. Brauer, H. Renner, A. Wernet, Z. anorg. Chem., 277, 249 (1954).